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TECHNICAL NOTE

CORRELATION EFFECTS IN THE ALTERNANT

MOLECULAR ORBITAL APPROXIMATION

by

William H. Adams

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For Research in Atomic, Molecular and Solid-State Theory
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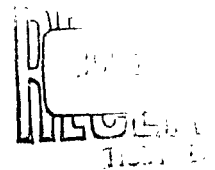
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ABSTRACT

Examination of the two electron density matrix in the
alternant molecular orbital approximation for a large system
in a singlet state, reveals that there are both short and long
range correlations between the electrons of opposite spin. There
is also a long range correlation between electrons of the same
spin. These correlations are not found when the wave func-
tion for the system is approximated by a single determinant
of alternant molecular orbitals.

1. INTRODUCTION

One of the more practical methods that has been suggested for including some correlation between electrons in a system of many electrons, is Löwdin's alternant molecular orbital (AMO) method.[1] In this paper, we show that using the AMO method for a large system in a singlet state, it is possible to give general and easily interpreted formulas for the spin components of the one and two electron density matrices. Examination of the spin components of the two electron density matrix, reveals both short and long range correlations between electrons of opposite spin, and a long range correlation between electrons of like spin in addition to the short range statistical correlation, or Fermi hole. Our discussion serves to emphasize the differences between the spin properties of approximate wave functions which are eigenfunctions of the total spin angular momentum operator S^2 and those which are not.

In the next section we briefly describe the properties of AMO's and then write out formulas for the spinless one and two electron density matrices of a system of many electrons in a singlet state. In Section 3 we define correlation functions for electrons of like and opposite spin, and give the formulas for these correlation functions in a system of many electrons in the AMO approximation. The physical significance of these formulas is discussed. Appendix A contains exact formulas for the one and two electron density matrices in terms of the two fundamental invariants of the AMO method. Appendix B contains a discussion of the limited usefulness of the approximate formulas for the density matrices introduced in Section 2.

2. THE ONE AND TWO-ELECTRON DENSITY MATRICES

The AMO method involves two fundamental invariants,[1] which are defined in terms of two sets of orthonormal orbitals a_K and $\bar{a}_K$. In a system of $N = 2n$ electrons, there are n orbitals in each set. The $2n$ orbitals are required to satisfy the further orthogonality relation $(a_K | \bar{a}_L) = \lambda \delta_{KL}$. The fundamental invariants are $\rho = \Sigma_K a_K a^*_K$ and

$\bar{\rho} = \Sigma_K \bar{a}_K \bar{a}^*_K$. (The AMO method can be generalized by allowing λ to depend on K .[2] In this case it is required that the 2n orbitals be linearly independent). In the AMO method for singlet states, the a_K are assigned up spin, the $\bar{a}_K$, down spin. From these N spin orbitals one constructs the AMO wave function for a singlet state of an N electron system by taking the singlet projection of a determinant of these spin orbitals. The spinless one and two elec-tron density matrices can be derived from the general expressions which have been given for the expectation values of one and two elec-tron operators, using the AMO, singlet state wave function.[3] If we assume that $\lambda^{2n} \ll n^{-1} \ll 1$ and neglect as small all terms of the first order and higher in n^{-1} , we obtain the following expressions for the spinless density matrices:

$$P_1(1;1') = \rho(1|1') + \bar{\rho}(1|1') \tag{1}$$

$$P_2(12;1'2') = P_1(1;1')P_1(2;2') - \rho(1|2')\rho(2|1') - \bar{\rho}(1|2')\bar{\rho}(2|1')$$

These are exactly the expressions one obtains from the unprojected single determinant of AMO's. One cannot conclude from this that for n → ∞ , the single determinant of AMO's and its singlet projec-tion are degenerate, however. We discuss this point in Appendix B.

The correlation energy in the Hartree-Fock (HF) approxima-tion is due mainly to the lack of correlation between electrons of opposite spin.[4] Thus we want to show that the AMO method intro-duces such a correlation. The physical idea behind the AMO method is that by assigning electrons of opposite spin to orbitals localized on different sublattices of the alternant system, one insures that on the average the electrons are further apart. (An alternant system is one whose lattice can be constructed from two equivalent, inter-penetrating sublattices). In the AMO method ρ is large about the nuclei of one sublattice, $\bar{\rho}$ about the nuclei of the other sublattice.

3. ELECTRON CORRELATION

Before we can properly discuss correlation between the elec-
trons, we must discuss the one-electron density matrix. We have
given a formula for the spinless one-electron density matrix. One might
from this formula naively conclude that ρ gave the density of up spin
electrons, and $\bar{\rho}$, the density of down spin electrons. This is just the
result one would have gotten if one had not taken the singlet projection
of the determinant. [We know of course that $P_1(1; 1') = P_1(\overset{+}{1}; \overset{+}{1}') +$
$+ P_1(\bar{1}; \bar{1}')$, i.e., the one-electron density matrix is the sum of an up
spin density matrix and a down spin density matrix. We have adopted
the notation of McWeeny and Mizuno[5] for the spin components of the den-
sity matrices]. It is well known that in a singlet state the spin density
is zero everywhere[5], i.e., $P_1(\overset{+}{1}; \overset{+}{1}') = P_1(\bar{1}; \bar{1}')$. Thus the density of
up or down spin electrons is just $1/2(\rho + \bar{\rho})$. This suggests that the
use of an unprojected determinantal wave function of AMO's will give
misleading results concerning the spin properties of the system,
although it may give a quite accurate result for the energy.[6,7]

For our purposes it is sufficient to define two correlation func-
tions,

$$g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}'\overset{-}{2}') = P_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}'\overset{-}{2}') - P_1(\overset{+}{1}; \overset{+}{1}') P_1(\overset{-}{2}; \overset{-}{2}')$$

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In other words, we say that two particles A and B are uncorrelated when
A is at point r_A and B is at point r_B, if the probability of that con-
figuration is equal to the product of the probability of finding A at r_A
and the probability of finding B at r_B. To obtain the correlation func-
tions we have defined, we need some spin components of the two-electron
density matrix. Fortunately for the singlet state they are easily obtained
from the spinless two-electron density matrix by using McWeeny's and
Mizuno's Eqs. (3.2) and (3.5).[5] This leads to the following expression:

$$g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}\overset{-}{2}) = -(12)^{-1}\sigma(1/1)\sigma(2/2) - (6)^{-1}|\sigma(1/2)|^2 \tag{2}$$

$$\sigma(1/2) = \rho(1/2) - \bar{\rho}(1/2)$$

For $\underline{r}_1 = \underline{r}_2$, one sees that $g_2(\overset{+}{1}\overset{-}{1}; \overset{+}{1}\overset{-}{1}) = -\frac{1}{4}|\sigma(1|1)|^2 \leqslant 0$. Thus the electrons of opposite spin are correlated at very short distances. One feels that this is the energetically important correlation. From the unprojected determinant one finds $g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}\overset{-}{2}) \equiv 0$, i.e., the electrons of opposite spin are uncorrelated in a formal sense, although the energy per electron in a many electron system is approximately equal to that of the singlet projection. One can argue that to discuss correlation between electrons of opposite spin using an unprojected determinantal wave function is not meaningful since the eigenfunctions of a spinless Hamiltonian must be spin eigenfunctions. This is consistent with our observation on the properties of the one-electron density matrix.

In addition to the short range correlation between the electrons, there is also a long range correlation. For $|\underline{r}_1 - \underline{r}_2|$ so large that $\rho(1|2)$ and $\bar{\rho}(1|2)$ are negligibly small in comparison to $\rho(1|1)$ and $\bar{\rho}(1|1)$, the correlation functions are related,

$$g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}\overset{-}{2}) \cong -(12)^{-1}\sigma(1|1)\,\sigma(2|2) \cong -g_2(\overset{+}{1}\overset{+}{2}; \overset{+}{1}\overset{+}{2}) \qquad (3)$$

The physical meaning of this equation is easily extracted by recalling the properties of ρ and $\bar{\rho}$ in alternant systems. If we choose $\underline{r}_1$ so that $\rho(1|1)$ is a maximum, $g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}\overset{-}{2})$ has a maximum wherever $\bar{\rho}(2|2)$ has a maximum, and $g_2(\overset{+}{1}\overset{+}{2}; \overset{+}{1}\overset{+}{2})$ has a maximum wherever $\rho(2|2)$ has a maximum. If $\underline{r}_1$ is chosen so that $\bar{\rho}(1|1)$ is a maximum, then $g_2(\overset{+}{1}\overset{-}{2}; \overset{+}{1}\overset{-}{2})$ has a maximum wherever $\rho(2|2)$ has a maximum, and $g_2(\overset{+}{1}\overset{+}{2}; \overset{+}{1}\overset{+}{2})$, wherever $\bar{\rho}(2|2)$ has a maximum. Thus in this relative sense, electrons of one spin are localized on one sublattice of an alternant system, electrons of the other spin on the other sublattice.

Although we have explicitly used the AMO approximation in the preceding discussion, similar conclusions would be reached if one took the singlet projection of an unrestricted Hartree-Fock (UHF) wave function.[8] In that case, however, one would not be able to say in general that the electrons of opposite spin were localized on different sublattices of the system, i.e., you would need information about the ρ and $\bar{\rho}$ of the UHF approximation.

In conclusion, we remark that the results of this paper provide a physical understanding of the AMO wave functions which the author has considered for the electron gas.[9]

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$$g_2(\overset{+-}{12}; \overset{+-}{12}) \cong -(12)'\sigma(1|1)\,\sigma(2|2) \cong -g_2(\overset{++}{12}; \overset{++}{12}) \qquad (3)$$

The physical meaning of this equation is easily extracted by recalling the properties of ρ and $\bar{\rho}$ in alternant systems. If we choose $\underline{r}_1$ so that $\rho(1|1)$ is a maximum, $g_2(\overset{+-}{12}; \overset{+-}{12})$ has a maximum wherever $\bar{\rho}(2|2)$ has a maximum, and $g_2(\overset{++}{12}; \overset{++}{12})$ has a maximum wherever $\rho(2|2)$ has a maximum. If $\underline{r}_1$ is chosen so that $\bar{\rho}(1|1)$ is a maximum, then $g_2(\overset{+-}{12}; \overset{+-}{12})$ has a maximum wherever $\rho(2|2)$ has a maximum, and $g_2(\overset{++}{12}; \overset{++}{12})$, wherever $\bar{\rho}(2|2)$ has a maximum. Thus in this relative sense, electrons of one spin are localized on one sublattice of an alternant system, electrons of the other spin on the other sublattice.

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ACKNOWLEDGEMENTS

APPENDIX A

Exact Formulas for P_1 and P_2 for the Singlet State

In addition to ρ and $\bar{\rho}$, we introduce the functions

$$\omega(1|2) = \int d\underline{r}_3 \, \rho(1|3) \, \bar{\rho}(3|2), \tag{A1}$$

$$\overline{\omega}(1|2) = \left[\omega(2|1)\right]^{*} \tag{A2}$$

The spinless one-electron density matrix is

$$P_1(1;1') = f_1(\lambda^2)\left[\rho(1|1') + \bar{\rho}(1|1') + f_2(\lambda^2)\left[\omega(1|1') + \overline{\omega}(1|1')\right]\right] \tag{A3}$$

$$f_1(\lambda^2) = n^{-1}(1-\lambda^2)^{-1}(1-\lambda^{2n+2})^{-1}\left[n - (n+1)\lambda^2 + \lambda^{2n+2}\right] \tag{A4}$$

$$f_2(\lambda^2) = n^{-1}(1-\lambda^2)^{-1}(1-\lambda^{2n+2})^{-1}\left[1 - (n+1)\lambda^{2n} + n\lambda^{2n+2}\right] \tag{A5}$$

The spinless two-electron density matrix is

$$P_2(12;1'2') = f_3(\lambda^2)\left\{\left[\rho(1|1') + \bar{\rho}(1|1')\right]\left[\rho(2|2') + \bar{\rho}(2|2')\right] - \right.$$

$$+ f_4(\lambda^2)\left\{\rho(1|2')\bar{\rho}(2|1') + \bar{\rho}(1|2')\rho(2|1')\right.$$
$$+ \left[\rho(1|1') + \bar{\rho}(1|1')\right]\left[\omega(2|2') + \overline{\omega}(2|2')\right]$$
$$+ \left[\omega(1|1') + \overline{\omega}(1|1')\right]\left[\rho(2|2') + \bar{\rho}(2|2')\right]$$
$$- \left[\rho(1|2') + \bar{\rho}(1|2')\right]\left[\omega(2|1') + \overline{\omega}(2|1')\right]$$
$$- \left[\omega(1|2') + \overline{\omega}(1|2')\right]\left[\rho(2|1') + \bar{\rho}(2|1')\right]$$
$$+ \left.\omega(1|2')\overline{\omega}(2|1') + \overline{\omega}(1|2')\omega(2|1')\right\}$$
$$+ f_5(\lambda^2)\left\{\omega(1|1')\omega(2|2') + \overline{\omega}(1|1')\omega(2|2')\right.$$
$$- \tfrac{1}{2}\omega(1|2')\omega(2|1') - \tfrac{1}{2}\overline{\omega}(1|2')\overline{\omega}(2|1')\right\} \tag{A6}$$

$$f_3(\lambda^2) = n^{-1}(n-1)^{-1}(1-\lambda^2)^{-2}(1-\lambda^{2n+2})^{-1} \times$$
$$\times \left[n(n-1) - 2(n^2-1)\lambda^2 + n(n+1)\lambda^4 - 2\lambda^{2n+2} \right] \tag{A7}$$

$$f_4(\lambda^2) = n^{-1}(n-1)^{-1}(1-\lambda^2)^{-2}(1-\lambda^{2n+2})^{-1} \times$$
$$\times \left[n-1 - (n+1)\lambda^2 + (n+1)\lambda^{2n} - (n-1)\lambda^{2n+2} \right] \tag{A8}$$

$$f_5(\lambda^2) = 4n^{-1}(n-1)^{-1}(1-\lambda^2)^{-2}(1-\lambda^{2n+2})^{-1} \times$$
$$\times \left[2 - n(n+1)\lambda^{2n-2} + 2(n^2-1)\lambda^{2n} - n(n-1)\lambda^{2n+2} \right] \tag{A9}$$

APPENDIX B

Validity of Formulas for P_1 and P_2 for the Case of Large n

Assuming that $\lambda^{2n} \ll n^{-1} \ll 1$, one finds to order n^{-2},

$$f_1(\lambda^2) = 1 - n^{-1}(1-\lambda^2)^{-1}\lambda^2$$
$$f_2(\lambda^2) = n^{-1}(1-\lambda^2)^{-1} \tag{B1}$$

$$f_3(\lambda^2) = 1 - 2n^{-1}(1-\lambda^2)^{-1}\lambda^2 + 2n^{-2}(1-\lambda^2)^{-2}\lambda^4$$
$$f_4(\lambda^2) = n^{-1}(1-\lambda^2)^{-1} - 2n^{-2}(1-\lambda^2)^{-2}\lambda^2$$
$$f_5(\lambda^2) = 4n^{-2}(1-\lambda^2)^{-2} \tag{B2}$$

If we write P_1 as a power series in n^{-1}, then to order n^{-2}

$$P_1 = P_1^{(0)} + n^{-1}P_1^{(1)} \tag{B3}$$

(In Eq. (1) we took the limit $n \to \infty$, so that the P_1 given there corresponds to $P_1^{(0)}$ in the above equation.) From Eq. (A3) we see that term

by term $P_1^{(1)}$ is proportional to the electron density. Integrated over all space $P_1^{(1)}$ gives zero, as is implied by the expansion in n^{-1}. (The trace of $P_1^{(0)}$ is equal to $2n$). Thus $P_1^{(1)}$ corresponds to a charge distribution of zero net charge. To the expectation value of the nuclear coulomb potential, $n^{-1}P_1^{(1)}$ gives a contribution independent of n since the number of nuclei is proportional to n. (If the trace of $P_1^{(1)}$ were proportional to n as a term by term inspection of $P_1^{(1)}$ would imply, then it would contribute to the expectation value of the sum of the nuclear coulomb potentials, a term proportional to n. On the other hand to the trace of P_1 it would contribute a term independent of n, which would be negligibly small in comparison to the trace of $P^{(0)}$ for large n. This suggests that the direct, numerical calculation of density matrices for many electron systems could give expectation values in error by terms proportional to the total number of electrons, although the error in normalization would be negligibly small).

A similar analysis may be carried through for P_2. In that case the part of $P_2^{(1)}$ which is term by term of the order of magnitude of the electron density squared, can be factored into two parts. The one part is a charge distribution of zero net charge, the other has a net charge proportional to n. Thus $P_2^{(1)}$ contributes to the total energy a term independent of n for the singlet state.

FOOTNOTES

1. P.O. Löwdin, Symposium on Molecular Physics (Maruzen, Tokyo, Japan, 1953), p. 13; Phys. Rev. 97, 1509 (1955).

2. This generalization has been discussed recently by J. de Heer, J. Chem. Phys. 37, 2080 (1962).

3. R. Pauncz, J. de Heer and P.O. Löwdin, J. Chem. Phys. 36, 2247 (1962).

4. J.E. Lennard-Jones, J. Chem. Phys. 20, 1024 (1952).

5. R. McWeeny and Y. Mizuno, Proc. Roy. Soc. (London) A259, 554 (1961).

6. Criticisms of the use of the unrestricted Hartree-Fock method in computing spin densities have been given recently by R.F. Wood and K.F. Berggren (Phys. Rev. to be published).

7. See, however, the discussion given by W. Marshall, Proc. Phys. Soc. 78, 113 (1961).

8. F. Sasaki (private communication) and P.O. Löwdin (private communication).

9. One such wave function has been described briefly in Section 5 of a paper by the author. [Phys. Rev. 127, 1650 (1962)].

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